

UNITED STATES PATENT OFFICE

2,653,085

ETCHING SOLUTION AND PROCESS

Richard H. Wynne, Jr., Pittsburgh, Pa., assignor
to Westinghouse Electric Corporation, East
Pittsburgh, Pa., a corporation of Pennsylvania

No Drawing. Application August 9, 1952,
Serial No. 303,610

6 Claims. (Cl. 41—42)

1

This invention relates to a novel etching solution and process for preparing the surface of metals and metalloids such as germanium and silicon for use in semiconductor devices such as rectifiers and transistors.

In such devices, the most desirable characteristics are obtained only if the germanium surface is given a suitable preparatory treatment. This treatment involves cutting a section, as for instance a wafer, from an ingot of germanium, grinding the surface to a dull gray finish with a suitable wet abrasive powder, washing and drying the surface, and then etching the surface in a suitable etchant solution until the dull, lustreless gray appearance has been replaced by a surface having a sharply delineated grain structure and a metallic lustre on the grain surfaces. Suitable electrodes are then applied to the treated surface. The device is then subjected to an electrical "forming" operation well known to those skilled in the art.

The etchant solution used in this treatment has a considerable effect upon the characteristics of the finished device. Prior to this invention, an etchant solution commonly used was an aqueous solution of nitric acid, hydrofluoric acid and copper nitrate. In my experiments, I have discovered an etching process and solution that provides an etch on the surface of metal and metalloid bodies, such as germanium and silicon, which is far superior to that accomplished by the solution described above, as will be hereinafter shown.

Accordingly, an object of this invention is to provide an improved process for preparing the surface of a body of germanium for use in a semiconductor device by etching said surface in an aqueous solution of hydrofluoric acid, nitric acid, and silver nitrate.

A further object of this invention is to provide an improved etching solution, the essential ingredients of which comprises an aqueous mixture of hydrofluoric acid, nitric acid, and silver nitrate.

The aqueous solution of hydrofluoric acid, nitric acid and silver nitrate may be used effectively for etching germanium in a considerable range of proportions and dilutions. The etching solution of this invention comprises the following range of ingredients by weight; from 50% to 86% by weight of water and from 14% to 50% by weight of acid, the acids being present in ratios of hydrofluoric acid (HF) to nitric acid (HNO₃) of from 6:1 to 1:16 by weight, and silver nitrate being dissolved in the aqueous acid solution in an amount of at least 1% of the weight thereof.

2

Convenient commercial sources of the ingredients of the etching solution, as received from a supplier, are usually 48% to 50% hydrofluoric acid by weight having a specific gravity of 1.15; concentrated nitric acid which contains 70% to 72% by weight HNO₃ with a specific gravity of 1.42; and distilled water in which there has been dissolved a suitable weighed amount of silver nitrate.

Etching solution formulations giving good results have been made up having the following ratios in parts by volume using aqueous acid solutions as received from the supplier:

HF(50%):HNO₃(70%):H₂O=4:2:4

HF(50%):HNO₃(70%):H₂O=3:3:4

HF(50%):HNO₃(70%):H₂O=2:4:4

To each of the above three solutions was added an aqueous solution of silver nitrate to provide 0.200 g. of silver nitrate per 10 ml. total volume of aqueous acid solution.

A germanium body upon being immersed for one minute in any of the above etching solutions had a brilliant specular surface with sharply delineated grain boundaries. When viewed by reflected light, some grains appeared light while others appeared dark. When the angle of the surface or the angle of the incident light was changed, the bright and dark areas were reversed. This characteristic is termed metallic lustre.

The extent to which the total mixed acid volume, as received from the supplier, may be diluted with water ranges from 8 volumes acid: 2 volumes water to 5 volumes acid: 20 or more volumes water. The etching time required increases with the dilution. The practical limitation of dilution is reached when silver deposited on the germanium surface fails to redissolve in the mixed acids.

The silver nitrate may range from its maximum solubility in the diluted mixed acids down to approximately 0.10 g. in a total volume of 10 ml., such last concentration being approximately 1% by weight. Below this value, especially at approximately 0.05 g. and less per 10 ml. of a mixed acid solution, the depth of etching becomes too great even in a short time of 15 seconds.

The ratio of concentrated hydrofluoric acid to nitric acid by volume, as received from the supplier, may be varied from 9:1 to 1:9 if diluted with the proper amount of water to keep the action at a reasonable speed, in other words, to produce the desired etched surface in one minute.

Immediately upon removal from the etching

3

solution, the etched germanium body is thoroughly washed and dried, as by washing it in a running stream of cold water and then drying in an air blast.

It was found that the germanium bodies etched in the above manner gave a much sharper etch than the germanium bodies etched in the conventional hydrofluoric acid, nitric acid and copper nitrate solutions. With the silver nitrate as an additive, the crystal surface of the germanium body presented a number of facets all of which give Miller indices of (111). This was not true with the conventional etching solution hitherto known, having copper nitrate as an additive. The copper nitrate etchant gave Miller indices of (111) only when the surface being etched was approximately a (111) surface prior to immersion.

It has also been discovered that a germanium body etched with a solution having copper nitrate as an additive causes a far greater rate of decay of minority carriers than does a germanium body etched with a solution having silver as an additive. This means that when holes are injected into an N-type germanium sample, they will last much longer if a solution with silver nitrate as an additive has been used, than they would if copper nitrate had been used. Thus, it follows that an emitter in a transistor will be more efficient when a silver nitrate etchant is used than when a copper nitrate etchant is used.

Further, it has been found that germanium etched with a solution having silver nitrate as an additive provides a microscopic roughness on the surface of the germanium body which is not obtained with an etching solution having copper nitrate as an additive. With this added degree of roughness, contact probes used in making up a transistor device do not have a tendency to slide on the surface of the treated germanium body.

While the etching solutions and process disclosed herein are particularly directed to treating germanium, it is to be understood that they are equally applicable in treating silicon.

The description of the invention above is intended to be illustrative of and not in limitation on the scope of the invention.

What is claimed is:

1. The process of preparing the surface of a body of germanium for use in a semiconductor device which comprises etching said surface in an aqueous solution of hydrofluoric acid, nitric acid, and silver nitrate, and then washing said etching solution from said surface.

4

2. The process of claim 1 wherein the proportions of ingredients present in 100 parts by weight of etching solution comprises a mixture of from 50% to 86% by weight of water and from 14% to 50% by weight of acids, the acids being present in ratios of HF to HNO_3 of from 6:1 to 1:16 by weight, and silver nitrate being dissolved in the solution in an amount of at least 1% of the weight of the aqueous acid solution.

3. A solution for etching the surface of a semiconductor body in preparation for use in a semiconductor device in which 100 parts by weight of the solution is an aqueous acid mixture comprising 50% to 86% by weight of water, and 14% to 50% by weight of acids, the acids being hydrofluoric acid and nitric acid, the ratio of HF to HNO_3 varying from 6:1 to 1:16 by weight and silver nitrate being dissolved in the solution in an amount of at least 1% of the weight of the aqueous acid mixture.

4. In the process of preparing the surface of a body of germanium for use in a semiconductor device, the surface having substantially no portion with oriented Miller indices of (111), comprising etching the surfaces in an aqueous solution comprising a mixture of from 50 to 86% by weight of water and from 14% to 50% by weight of acids, the acids being present in ratios of HF to HNO_3 of from 6:1 to 1:16 by weight, and silver nitrate being dissolved in the solution in an amount of at least 1% of the weight of the aqueous acid solution, the etching being out for a period of time of the order of 15 seconds to one minute whereby the surface comprises a large proportion of facets having Miller indices of (111), and then washing the etching solution from said surface.

5. A germanium crystal having an etched probe surface with microscopic roughness derived by the process of claim 4.

6. A germanium crystal having an etched surface cut from the crystal at an orientation other than at a Miller index of (111), the etched surface comprising a large proportion of facets having Miller indices of (111), thereby being of microscopic roughness improving its cooperation with contact probes.

RICHARD H. WYNNE, JR.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,514,879	Lark-Horvitz	July 11, 1950